

1917
B73

Bramlet

Action of the Grignard Reagent on Thiocyanates

ACTION OF THE GRIGNARD REAGENT ON THIOCYANATES

BY

HUBERT B. BRAMLET

Butler

THESIS

FOR THE

DEGREE OF BACHELOR OF ARTS

IN

GENERAL SCIENCE

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1917

1917
B73

UNIVERSITY OF ILLINOIS

May 31 1917

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

HUBERT B. BRAMLET

ENTITLED ACTION OF THE GRIGNARD REAGENT ON THIOCYANATES

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF ARTS

In GENERAL SCIENCE

Roger Adams.

Instructor in Charge

APPROVED :

W. S. Royce

HEAD OF DEPARTMENT OF CHEMISTRY

376378

UNIVERSITY OF ILLINOIS - CHICAGO

1964

THE UNIVERSITY OF ILLINOIS - CHICAGO, CHICAGO, ILLINOIS 60607

DEPARTMENT OF CHEMISTRY

RECEIVED

FROM

DATE

BY

REMARKS

ANALYST

DATE

INITIALS



ACKNOWLEDGMENT

The writer wishes to take this opportunity for expressing his gratitude to Doctor Roger Adams for his cooperation and helpful suggestions throughout the course of this investigation.



Digitized by the Internet Archive
in 2013

<http://archive.org/details/actionofgrignard00bram>

TABLE OF CONTENTS

	Page
I. HISTORICAL AND THEORETICAL	1 - 7
II. EXPERIMENTAL	8 -18
III. CONCLUSION	19
IV. BIBLIOGRAPHY	20

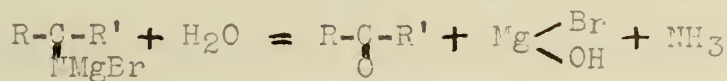
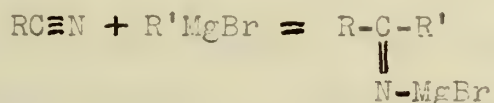
ACTION OF THE GRIGNARD REAGENT ON THIOCYANATES

I. HISTORICAL AND THEORETICAL

This investigation was undertaken at the suggestion of Roger Adams, under whose direction the work has been done. The scientific study of the reaction was first advanced in an article by Adams and Beebe.¹

Reactions of the Grignard reagent with many types of carbonyl containing compounds have been carefully and exhaustively studied, but this cannot be said concerning the reactions of the Grignard reagent with organic substances containing the radical $-C\equiv N$.

Blaise² treated cyanogen and certain aliphatic and aromatic nitriles with alkyl and aryl magnesium halides, and found that he obtained ketones according to the following equations:



With phenyl nitrile and ethyl magnesium bromide, an eighty per cent yield of the phenyl ethyl ketone was obtained, but much poorer yields were obtained with nitriles of the type of benzyl cyanide.

Fair yields of nitriles were obtained by Grignard³ who allowed a molecule of alkyl or aryl magnesium halide to drop into a molecule of chlorocyan.



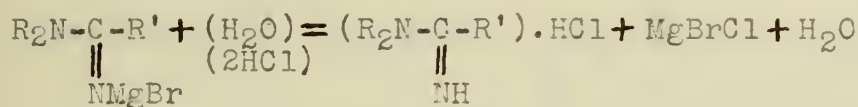
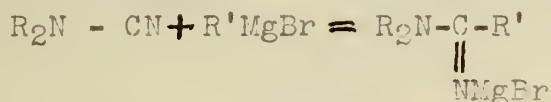
Cyanogen bromide and iodide are not suitable for this purpose; with the latter, entirely

$\text{RMgBr} + \text{ICN} = \text{RI} + \text{MgBrCN}$, while with BrCN , reactions of both types occur, the latter predominating.

By the same method of procedure with cyanogen, Grignard⁴ was able to produce nitriles instead of ketones, which Blaise obtained when he treated the Grignard reagent with cyanogen.



Adams and Beebe¹ studied the reaction on dibenzyl cyanamide and found that the reaction first gave a magnesium halide addition compound, which on decomposition with dilute acid, yielded the salts of substituted amidines.



It has been the purpose of our work to study the reaction of the Grignard reagent on organic compounds containing the $-\text{S}-\text{C}\equiv\text{N}$ radical. With one exception, all the reactions were carried out using the benzyl thiocyanate. We treated in ether solution ethyl, phenyl, and isobutyl magnesium bromides with a dry ether solution of the benzyl thiocyanate. Also the reaction of para-chlorobenzyl thiocyanate on ethyl magnesium bromide was carried out. The usual precautions for the exclusion of moisture and carbon dioxide were observed.

At first, the reaction was tried with ethyl magnesium bromide and benzyl thiocyanate, using small amounts and varying the

method of addition as well as the decomposition of the reaction-product. The proportions used were benzyl thiocyanate, 1 part; Mg, 1.2 parts; C_2H_5Br , 1.4 parts. Later it was found that better results were obtained by using three times the amount of magnesium and organic halide to one part of benzyl thiocyanate. The reaction product was decomposed with ice and hydrochloric acid, the ether layer was separated from the water and acid layer, and extracted several times with ether. The ethereal solution was dried over anhydrous sodium sulphate, and the ether distilled from a small distilling flask, adding the ethereal solution in small portions by means of a dropping funnel.

The substances obtained from this reaction-product proved to be benzyl mercaptan,  CH_2SH , thioethers  CH_2S-R' ,

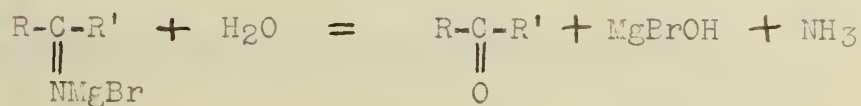
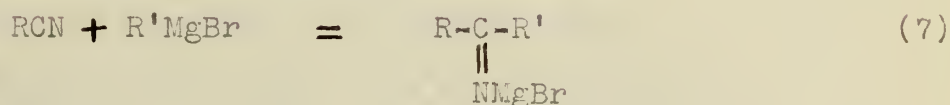
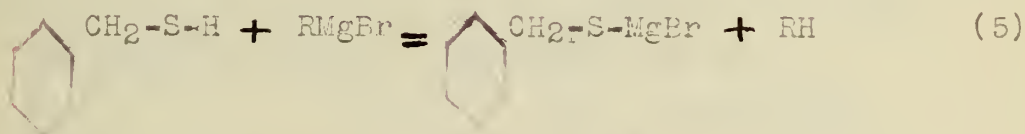
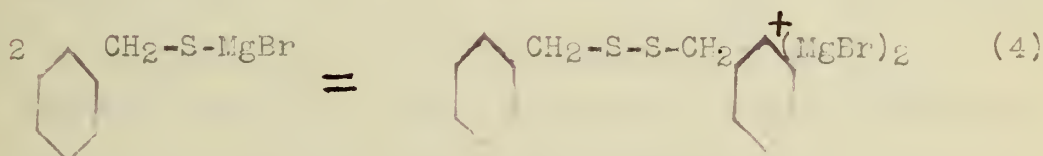
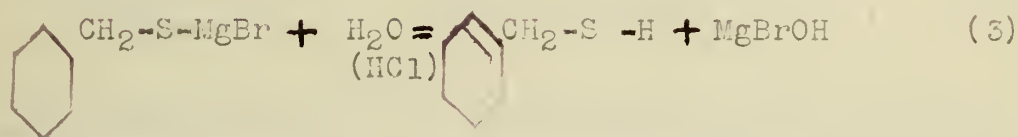
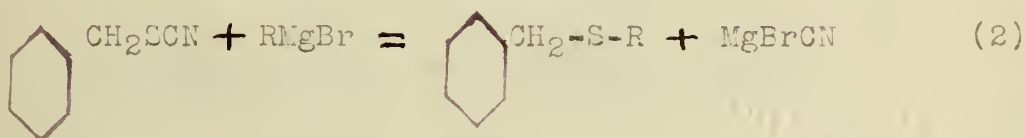
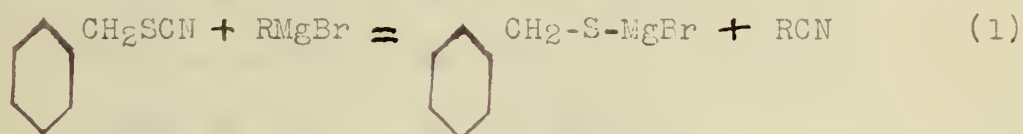
and in some cases dibenzyl disulphide,  $CH_2-S-S-CH_2$  and
m.p. 72°

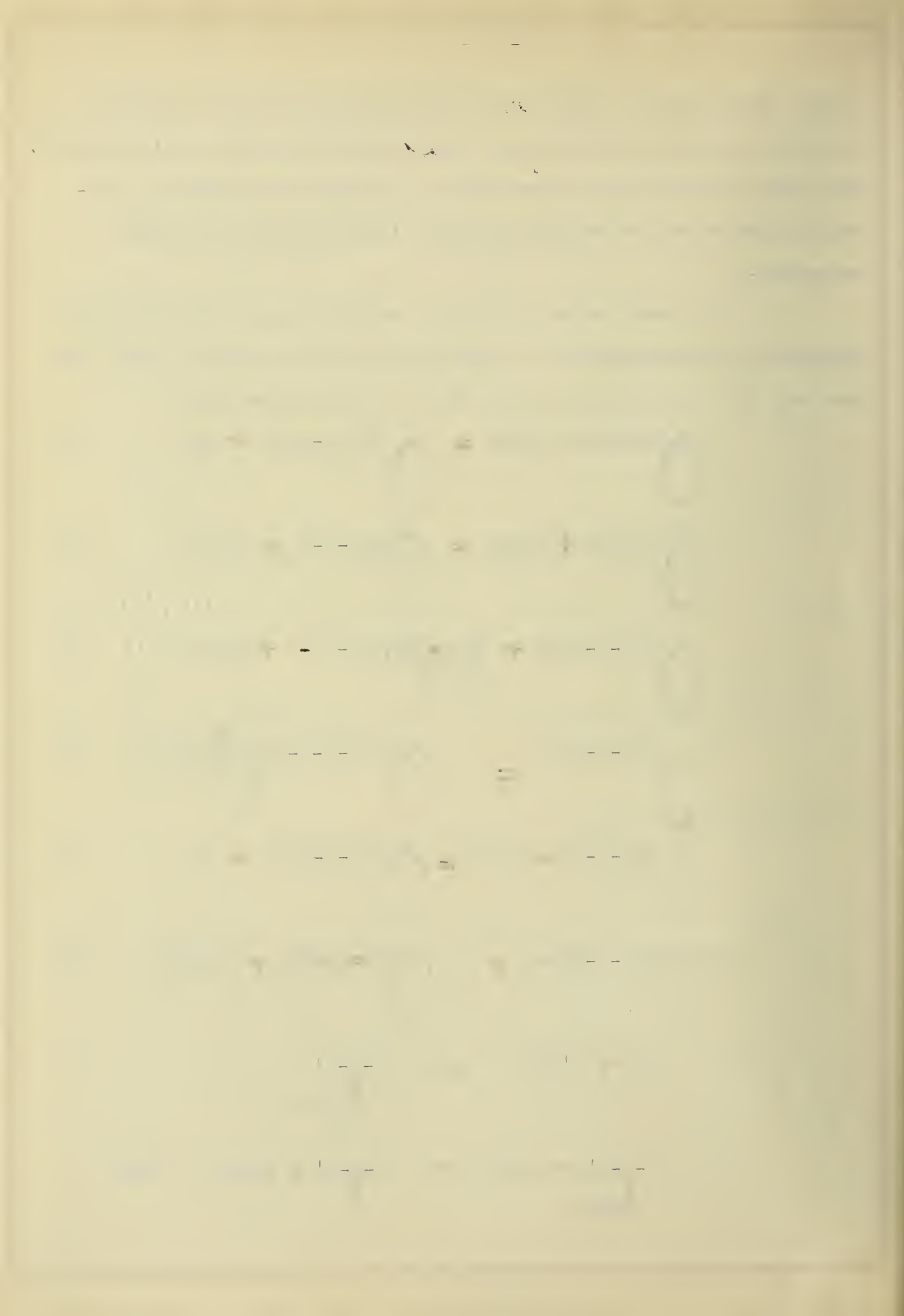
stilbene,  $CH=CH$ 
m.p. 124°

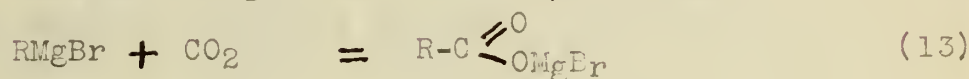
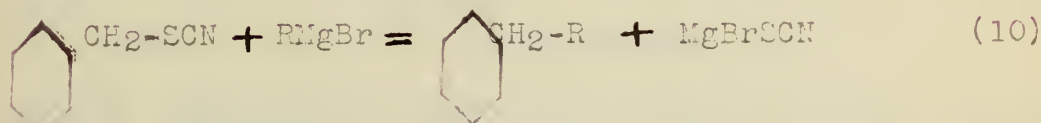
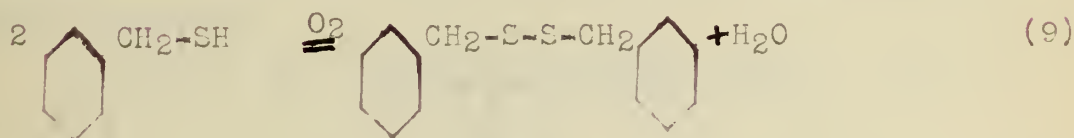
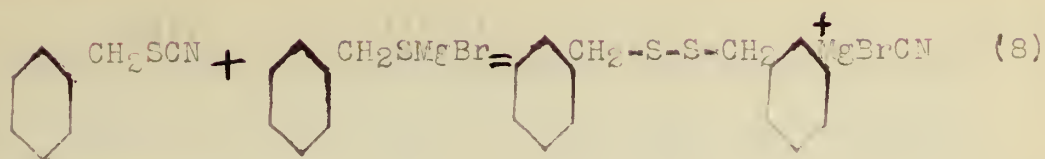
Fair yields of the mercaptan and thioethers were obtained in the case of ethyl magnesium bromide and benzyl thiocyanate, when the latter was added to a large excess of the Grignard reagent. With phenyl magnesium bromide, the phenyl benzyl sulfide was not formed but a large amount of benzophenone was obtained. With isobutyl magnesium bromide, the thioether was the main product. In the reactions with benzyl thiocyanate and ethyl magnesium bromide, when the ethereal solution was separated from the solid residues before decomposition,

it was found that the thioether was obtained from the ethereal solution and that the mercaptan was obtained from the solid residue. This would indicate the formation of a complex salt which on decomposition with ice and hydrochloric acid yields the benzyl mercaptan.

It seems to us that this reaction may be used for the preparation of mercaptans and thioethers and our results show that they may be formed according to the following equations:





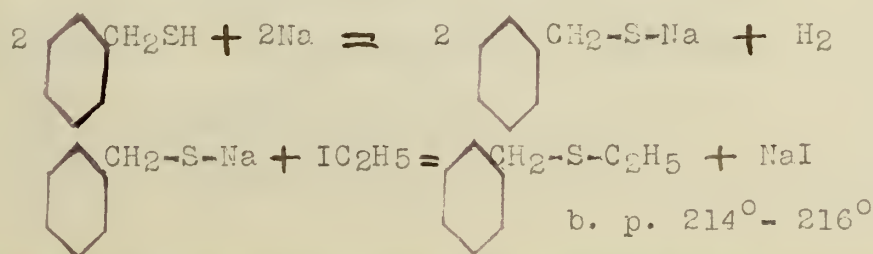


Among other methods for the preparation of mercaptans and thioethers, the following have been used in the past.

Märcker⁵ obtained benzyl mercaptan by the interaction of benzyl chloride and alcoholic potassium hydrogen sulfide.



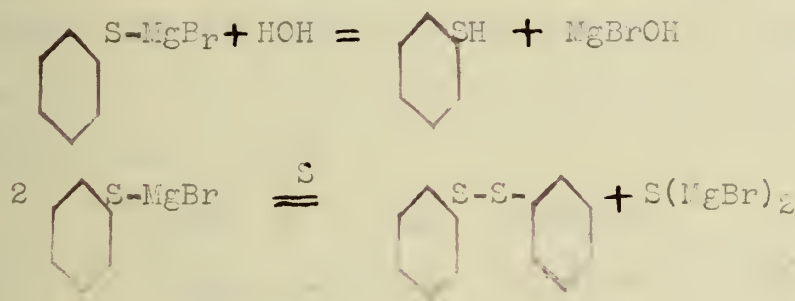
It is easily oxidized to dibenzyl disulfide, m. p. 66° - 67°. The same author⁶ prepared the benzyl ethyl sulfide by treating the sodium salt of benzyl mercaptan with ethyl iodide.



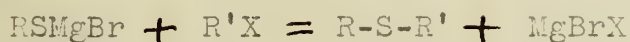
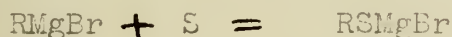
Carlson⁷ obtained quantitatively the benzyl phenyl sulfide by the interaction of benzyl nitrate with the potassium salt of phenyl mercaptan.



Taboury⁸ studying the reaction of finely divided sulphur on the Grignard reagent found that he obtained mercaptans and disulfides, according to the following equations:



Later, the same author⁹, studying the reaction of organic halides on the compound formed by the reaction of sulphur on the organo-magnesium halide, obtained a number of organic sulfides in yields of from 10 - 40%. The compounds obtained and the reaction may be summarized as follows:



Methyl phenyl sulfide, $\text{CH}_3\text{-S-C}_6\text{H}_5$, colorless liquid, b.p. 187°-190°

Ethyl " " $\text{C}_2\text{H}_5\text{-S-C}_6\text{H}_5$ " " b.p. 200°-206°

Benzyl " " $\text{C}_6\text{H}_5\text{-CH}_2\text{-S-C}_6\text{H}_5$ white leaflets m.p. 40°-41°

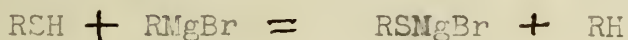
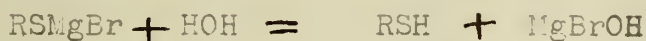
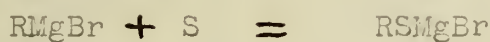
Methyl p.brom " " $\text{CH}_3\text{-S-C}_6\text{H}_4\text{Br}$ " crystals m.p. 32°

Benzyl p.brom " " $\text{C}_6\text{H}_5\text{CH}_2\text{-S-C}_6\text{H}_4\text{Br}$ " " m.p. 64°-65°

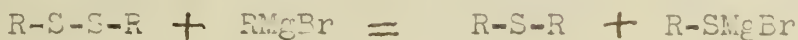
" p.chlor " " $\text{C}_6\text{H}_5\text{CH}_2\text{-S-C}_6\text{H}_4\text{Cl}$ " " m.p. 52°-53°

Ethyl p.cresol sulfide	$C_2H_5-S-C_6H_4CH_3$	b.p. $218^{\circ}-220^{\circ}$
Methyl α -naphthyl "	$CH_3-S-C_{10}H_7$	Colorless liquid, b.p. $166^{\circ}-168^{\circ}$ _{20mm.}
Ethyl α - " "	$C_2H_5-S-C_{10}H_7$	" " b.p. $175^{\circ}-176^{\circ}$ _{25mm.}
Benzyl α - " "	$C_6H_5CH_2-S-C_{10}H_7$	White leaflets m.p. $78^{\circ}-80^{\circ}$

Wuyts¹⁰ found that a thiol was the only product of the action of finely divided sulphur upon organo-magnesium compounds, if the reaction was carried out in an atmosphere of dry H_2 and care was taken to avoid excess of sulphur. The yield attained 80% of the theoretical. By the action of sulphur on the compound formed by the condensation of the thiol with an additional molecule of the reagent, a disulphide was formed:



while by the interaction of the disulfide and the organo-magnesium salt, a monosulfide was obtained:



II. EXPERIMENTAL

A. The reaction was first carried out using ethyl magnesium bromide and benzyl thiocyanate. The ethyl magnesium bromide was prepared in absolutely dry ether, using 1.2 and 1.4 excess of magnesium ribbon and ethyl bromide over the amount of benzyl thiocyanate to be used. The quantities used were as follows:

1 part of	$C_6H_5CH_2SCN$	20.0 grams
1.2 " "	Mg	3.9 "
1.4 " "	C_2H_5Br	20.44 "

The ethereal solution of the benzyl thiocyanate was cooled to $0^{\circ}C$ and was added slowly, by means of dropping funnel, to the cooled ethereal solution of the benzyl thiocyanate. The reaction flask was connected to an upright condenser, which was fitted at the top with a soda-lime tube for the exclusion of carbon dioxide and water. The temperature of the reaction flask was kept as low as possible by means of an ice mixture.

As the ethereal solution of the thiocyanate struck the Grignard reagent, a white solid would separate. The mixture stood for forty-eight hours at room temperature. The reaction flask and contents were cooled to $0^{\circ}C$ and it was decomposed with ice and concentrated hydrochloric acid. There was complete solution in both the ether and acid layers. The ether layer was separated, and the acid layer was extracted several times with ether. The ethereal solution was dried over anhydrous sodium sulphate and the ether was distilled off from a 50 c.c. distilling bulb, adding the ethereal solution in portions by means of a dropping funnel. After all the ether came over there was a yellow oil between 140° - 170° , amounting

to about five grams. It had a very disagreeable odor. At this point decomposition seemed to be taking place, so I distilled the remainder under a pressure of 68 m.m. A dark red oil was collected between 140° - 190° . A white solid crystallized from both the yellow and red oils. Upon recrystallization from ligroin its melting point was found to be 123° - 124° . This agrees with that of stilbene.

B. The substances and amounts used were the same as in the previous experiment, but the operation was reversed, adding the ethereal solution of the Grignard reagent to the ethereal solution of the benzyl thiocyanate. This time the contents of the reaction flask were not decomposed directly, but the ethereal solution was separated from the solid portion and distilled. Fractions were collected as follows:

First	20° - 35°	ether
Second	35° - 44°	mostly ether, 10 c.c.
Third	44° - 91°	clear oil, disagreeable odor very small amount

At this temperature, there remained a yellowish white solid, which represented the main portion of the reaction product. On further heating to 170° , decomposition took place and the solid turned red. I redissolved it in ether and attempted to recrystallize, but was unsuccessful, due to the presence of impurities.

C. This time like quantities of the reagents were used as in A and B and the Grignard reagent was added to the ethereal solution of the benzyl thiocyanate as in B. The ethereal solution was separated from the solid portion and distilled.

First	20° - 35°	ether
Second	35° - 63°	mostly ether, very small amount

This was all that would distill over from a water-bath, leaving a yellowish-white solid in the flask. This solid was dissolved in dry ether and the ether allowed to evaporate in a crystallizing dish. A yellowish-brown, pasty solid was left behind which formed a white solid residue upon burning on a platinum foil. This fact would indicate the formation of a magnesium salt. The solid in the dish was decomposed with ice and hydrochloric acid, with the formation of a yellow oil. This was extracted from the acid layer with ether, forming a green ethereal solution which was dried over anhydrous sodium sulphate.

This was separated from the sodium sulphate and the ether removed by distillation. The greenish black residual liquid was distilled from a 10 c.c. distilling bulb, using an air condenser. The temperature rose immediately to 225° and the major portion of the liquid came over between 225° - 228° . This quantity was too small to work with. The second portion was collected between 228° - 250° , where decomposition took place.

The solid portion from the reaction flask was decomposed with ice and hydrochloric acid. An oil was formed on top of the acid layer and this was extracted with ether, forming a yellow ethereal solution. It was dried over anhydrous sodium sulphate, after which the ether was distilled from a 50 c.c. distilling bulb as in A.

First	20° - 35°	ether
Second	35° - 90°	reddish oil. 2 c.c.
Third	90° - 180°	yellow oil. 3 c.c.

At this point a white solid began to separate in the flask.

Also some of the solid collected in the tube of the condenser. On further heating decomposition took place. The solid was pressed out on a clay plate and recrystallized from ligroin. Its melting point was found to be 122° - 123° .

D. In this reaction the amount of benzyl thiocyanate was increased to 50 grams, so that the quantities used were as follows:

1.0 part	$C_6H_5CH_2SCN$	50.0	grams
1.2 "	Mg	9.75	"
1.4 "	C_2H_5Br	51.1	"

Since the magnesium ribbon could not be obtained at this time, the powdered magnesium was used. Some difficulty was met in the preparation of the ethyl magnesium bromide and all of the magnesium powder was not used up in the reaction.

The Grignard reagent was added to the ethereal solution of the benzyl thiocyanate. A white, flocculent solid was formed on its addition, the reaction taking place rather violently. After the reaction was completed, the ethereal solution was poured off, the solid remaining in the flask. This ethereal solution was decomposed with ice and hydrochloric acid, and extracted several times with ether. After drying the ether was distilled over and a clear yellow oil was left behind. A light reddish oil came over at first, but the major part distilled between 223° - 230° . Some white solid also collected in the condenser. Above 230° decomposition took place. The second portion, boiling at 223° - 230° , was redistilled. About half of it came over in a pinkish oil below 222° , the temperature rising gradually. The portion between 222° - 230° was a red oil, and with the last portions of the oil, some more of the

solid was collected in the condenser.

The solid portion from the reaction flask was decomposed with ice and hydrochloric acid, and extracted several times with ether. The ethereal solution was dried with anhydrous sodium sulphate and the ether distilled off. A red oil was left in the distilling flask at this point. Between 45° - 58° a very small amount of liquid was obtained. The remaining portion was heated on the water-bath as high as 70° . In order to avoid the chances of decomposition this oil was placed in a weighing tube, corked and placed in an ice and salt bath. In a few minutes, the entire mass crystallized in a yellowish-white solid. The entire quantity was clay plated, forming almost white powdery crystals.

Weight of crystals	7 grams
--------------------	---------

M. p. of crude crystals	60° - 65°
-------------------------	-----------------------------

Recrystallized from alcohol in white powdery crystals. The first and larger portion of the crystal was filtered and dried. M. p. 71° . A second and third portion of crystals were also obtained from the mother liquor.

E. It was now decided to use a large excess of the Grignard reagent and to add the ethereal solution of the benzyl thiocyanate to the ethyl magnesium bromide. The quantities used were as follows:

1.0 part	$C_6H_5CH_2SCN$	40 grams
$1.2 \times 3 = 3.6$ part	Mg	23.4 "
$1.4 \times 3 = 4.2$ "	C_2H_5Br	122.6 "

The cooled ethereal solution of the benzyl thiocyanate was added to the cooled ethereal solution of the Grignard reagent. The reaction took place with considerable violence, a large amount of the greyish black, sticky residue separating in the bottom of the flask.

The ethereal solution was poured off from the sticky residue and decomposed with ice and hydrochloric acid. The ether layer was separated and dried over anhydrous sodium sulphate. The ether was removed by distillation and the crude product of yellow oil weighed 20 grams. Fractions were collected as follows:

First	35°-190°	small amount, ketone odor
Second	190°-231°	major portion (217°-231°) Small residue

The second portion was refractionated and the oil distilled over between 215°-217°. Weight, 7 grams.

The sticky residue from the reaction flask was decomposed with ice and hydrochloric acid, the oily layer was extracted with ether, and dried over anhydrous sodium sulphate. The ether was removed by distillation and the crude product of yellow oil weighed 18.5 grams. Fractions were collected as follows:

First	35°-87°	small amount
Second	87°-210°	major portion (190°-210°) Small residue

The second portion was refractionated and the oil distilled over between 195°-196°. Weight, 8 grams. In these fractionations a small 25 c.c. Ladenburg distilling bulb was used very successfully.

F. To check the previous reaction, it was carried out in the same manner, using a larger amount of the reagents. The quantities used were as follows:

1.0	part	$\text{C}_6\text{H}_5\text{CH}_2\text{SCN}$	50.0 grams
1.2x4 = 4.8	"	Mg	38.0 "
1.4x4 = 5.6	"	$\text{C}_2\text{H}_5\text{Br}$	204.4 "

The ethereal solution was filtered from the solid residue and de-

composed with ice and hydrochloric acid. The oily layer was extracted with ether until all was separated. After drying the ethereal solution with anhydrous sodium sulphate the ether was distilled over and the crude product weighed. Weight, 19.4 grams. After three fractionations, the major portion distilled over between 214° - 220° . Weight, 10 grams. Reading of barometer, 737 m.m. at 27°C .

The solid residue was decomposed with ice and hydrochloric acid and the oily layer was taken up in ether. After drying the ethereal solution, the ether was distilled over and the crude product weighed. Weight, 26.3 grams. After three fractionations, the major portion distilled over between 194° - 196° . Weight, 13 gms. A small portion between 213° - 217° was also obtained; weight 4 grams.

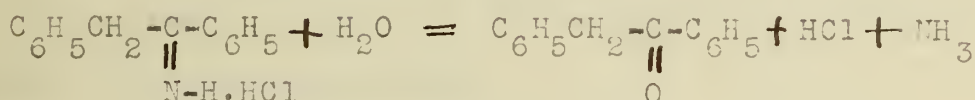
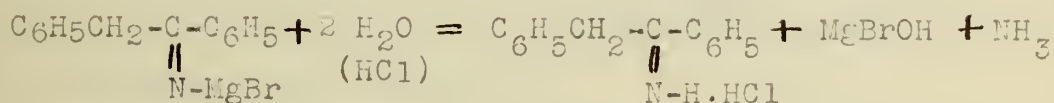
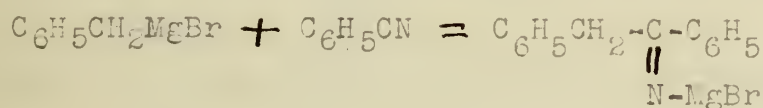
G. It was now decided to try the reaction with phenyl magnesium bromide. The quantities used were as follows:

1.0	part	$\text{C}_6\text{H}_5\text{CH}_2\text{SCN}$	50.0 grams
$1.2 \times 3 = 3.6$	"	Mg	29.4 "
$1.4 \times 3 = 4.2$	"	$\text{C}_6\text{H}_5\text{Br}$	249.5 "

The ethereal solution of benzyl thiocyanate was run into a large excess of the ethereal solution of phenyl magnesium bromide. The reaction was similar to the previous runs with ethyl magnesium bromide.

The reaction product was decomposed with ice and hydrochloric acid without separation of the solid portion, keeping the flask cool with an ice and salt mixture. The evolution of gas was not as large as in previous runs and there was not complete solution. Between the acid and ether layers there was a layer of white starchy

solid. This solid was filtered off with suction, washed with acid and water, refiltered, rewashed, dried and clay plated. It was placed in a weighing bottle and weighed. Weight, 7 grams. After standing over for three days another solid separated from the filtrate of the above. It was filtered off, washed with water, dried and clay plated. Weight, 5 grams. The latter is soluble in ether and its melting point was found to be 48°-49°. This agrees with benzophenone, m.p. 48°. So it is the result of the hydrolysis of the first solid, according to the following reactions:



The ether layer was separated completely from the water layer by several extractions. It was dried with anhydrous sodium sulphate and the ether evaporated from a water bath. The weight of the crude product was 144.5 grams. It was distilled under a pressure of 15 m.m.

First	35°-130°	clear oil, major portion 80°-90°
Second	130°-185°	green oil, major portion 160°-170°
		Weight, 33 grams

The second portion was redistilled under 17 m.m. pressure.

First	35°-165°	very small
Second	165°-175°	major portion 167°-170°
		Weight, 30 grams

This portion was seeded with a crystal of benzophenone, and

crystallized completely. The melting point of the purified crystals was 48° - 49° .

The first portion distilling 35° - 130° at 15 m.m. was fractionated under ordinary pressure. Second fractionation, 747.8 m.m. at 23° C.

First	70° - 150°	some benzene	7 grams
Second	150° - 160°	major portion 153° - 157°	33 grams
Third	160° - 190°		12 "
Fourth	190° - 200°	major portion 192° - 197°	11 "
Red oil above 200°			

The second fraction contains bromobenzene whose boiling point is 157° . The fourth fraction and most of the third represents the benzyl mercaptan, b.p. 194° - 195° .

So the main products of this reaction are benzophenone, bromobenzene, and benzyl mercaptan.

H. The reaction of the Grignard reagent was tried on para-chlorobenzyl thiocyanate. The latter was prepared by the bromination of p. chlorotoluene and subsequent treatment in absolute alcohol solution with ammonium thiocyanate. The portion used in the reaction was collected between 163° - 170° at 23 m.m. pressure. Its melting point is given as 17° C.¹¹ The quantities used were as follows:

1.0 part	$C_6H_4Cl-CH_2SCN$	25.0 grams
$1.2 \times 3 = 3.6$ parts	Mg	11.2 "
$1.4 \times 3 = 4.2$ "	C_2H_5Br	58.5 "

The dry ether solution of the p. chlorobenzyl thiocyanate was added to the ethereal solution of the Grignard reagent. The reaction product was decomposed with ice and concentrated hydrochloric acid, the oily layer was extracted several times with ether and dried over

anhydrous sodium sulphate. The ether was distilled over and the crude product of a reddish yellow oil weighed 33 grams. This was distilled under a pressure of 18 m.m.

First	68°-132°	small amount of liquid
Second	132°-183°	liquid at first, then solid, 12 gms
Third	183°-224°	yellow solid, 10 gms

This solid was re-crystallized from ligroin and its melting point was found to be 69°-71°. As yet, I have not been able to identify this solid. Failure may be attributed partially to the impurities in the p. chlorbenzyl thiocyanate.

I. The reaction was last tried with isobutyl magnesium bromide and benzyl thiocyanate. The quantities used were as follows:

1.0	part	$\text{C}_6\text{H}_5\text{CH}_2\text{SCN}$	25 grams
$1.2 \times 3 = 3.6$	"	Mg	14.7 "
$1.4 \times 3 = 4.2$	"	$(\text{CH}_3)_2\text{CHCH}_2\text{Br}$	96.0 "

The ethereal solution of the benzyl thiocyanate was added to a large excess of the isobutyl magnesium bromide. The reaction product was decomposed with ice and hydrochloric acid, extracted with ether, and the ethereal solution was dried with anhydrous sodium sulphate. The ether was removed by distillation. The weight of the crude product was 18 grams. After repeated fractionations the following fractions were collected:

First	110°-180°	small amount
Second	180°-210°	clear liquid, 4 grams
Third	210°-215°	small amount
Fourth	215°-240°	contains part of next fraction
Fifth	240°-245°	major portion, 243°-244° a reddish brown oil, 10 grams

Barometric pressure 737 m.m. at 27°C

The main products of this reaction seem to be benzyl mercaptan and an oil, the thioether, which I have identified as the isobutyl benzyl sulfide, b.p. 243°-244°.

The sulphur was determined by the method of Carius.

Weight of sample taken	0.1473 grams
------------------------	--------------

" " BaSO ₄ obtained	0.1823 "
--------------------------------	----------

Calc. for C₁₁H₁₆S: S, 17.77%. Found: S, 16.99%.

Index of Refraction at 20°C.

Readings	1.4910
----------	--------

	1.4912
--	--------

	1.4912
--	--------

	<u>1.4913</u>
--	---------------

Average	1.4912
---------	--------

D. 0.968 $\frac{20}{20}$.

III. CONCLUSION

1. In the study of the reaction of the Grignard reagent on thiocyanates, we found that dibenzyl disulfide and stilbene were the main products of the reaction, when the reacting substances were used in equi-molecular amounts.

2. When the ethereal solution of the benzyl thiocyanate was run into a large excess (3 mols) of the Grignard reagent, it was found that a mixture of benzyl mercaptan and the thioether, $C_6H_5CH_2-S-R$, was obtained.

3. With phenyl magnesium bromide and benzyl thiocyanate the main product of the reaction was benzophenone, with a small amount of the benzyl mercaptan.

4. By the interaction of isobutyl magnesium bromide and benzyl thiocyanate, the main product of the reaction was benzyl isobutyl sulfide.

5. A partial study of the reaction of the Grignard reagent on organic compounds containing the $-SCN$ radical has been made, resulting in a new method for the synthesis of mercaptans and thioethers.

6. With further study, the mechanism of the reactions and more extended applications of its use with other $-SCN$ compounds may be determined.

IV. BIBLIOGRAPHY

1. Jour. Am. Chem. Soc. Vol. 38, No. 12 (Dec.1916)
pp. 2768-72
2. Compt. rend., **132**, 38 (1901); **133**, 299.
3. Compt. rend., **152**, 388 (1911).
4. Compt. rend., 155, 44 (1912).
5. A. **136**, 75.
6. A. 140, 88.
7. Ber. 40, 4194.
8. Bull. Soc. Chim. Paris. (3) **29**, 761-65
or C. 1903, (2) 620.
9. Bull. Soc. Chim. Paris (3) **31**, 1183-88
or C. 1905, (1) 80.
10. Bull. Soc. Chim. (4) **5**, 405. (1909)
11. Ber. 11, 905; Am. 2, 91.

UNIVERSITY OF ILLINOIS-URBANA



3 0112 079097033